



# Unconventional spin topology in surface alloys with Rashba-type spin splitting

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The spins of a pair of spin-orbit split surface states at a metal surface are usually antiparallelly aligned, in accord with the Rashba model for a two-dimensional electron gas. By first-principles calculations and two-photon photoemission experiments we provide evidence that in the surface alloy Bi/Cu(111) the spins of an unoccupied pair of surface states are parallelly aligned. This unconventional spin polarization, which is not consistent with that imposed by the Rashba model, is explained by hybridization of surface states with different orbital character and is attributed to the spin-orbit interaction. Since hybridization is a fundamental effect our findings are relevant for spin electronics in general.

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## I. INTRODUCTION

In the emerging field of spin electronics, proposals for device applications often utilize the Rashba effect in a two-dimensional electron gas (2DEG),<sup>1</sup> thereby relying on the spin topology of the 2DEG's electronic states (e.g., Refs. 2–6). The structural inversion asymmetry, that is, the asymmetric confinement of the 2DEG, leads via spin-orbit (SO) interaction to a splitting in the dispersion relation of the free electrons,

$$\epsilon_{\pm}(\mathbf{k}) = \epsilon_0 + \frac{\hbar^2 \mathbf{k}^2}{2m^*} \pm \alpha |\mathbf{k}|, \quad \mathbf{k} = (k_x, k_y), \quad (1)$$

where  $m^*$  is the effective mass. The Rashba parameter  $\alpha$  comprises the strength of the atomic SO interaction and of the gradient of the confining potential in the  $z$  direction.<sup>7,8</sup> The splitting, quantified by the displacement  $\Delta k = 2|\alpha m^*|/\hbar^2$  of the band extrema in reciprocal space, shows up as two concentric circles in the momentum distribution. The spins of the two electronic states at energy  $\epsilon$  are (i) oppositely aligned, are (ii) lying within the  $xy$  plane, and are (iii) normal to the wave vector  $\mathbf{k}$ .<sup>9</sup> The spin polarization can therefore be written as  $\mathbf{P}_{\pm}(\mathbf{k}) = \pm (k_y, -k_x, 0)/|\mathbf{k}|$ , implying also  $|\mathbf{P}| = 100\%$  [Fig. 1(a)].<sup>10</sup>

The above paradigmatic spin topology is found to a large extent in semiconductor heterojunctions<sup>11</sup> and in surface states at (111) surfaces of noble metals, in particular in Au(111).<sup>12,13</sup> The surface states in surface alloys such as Bi/Ag(111) (Refs. 14–16) or Pb/Ag(111) (Refs. 16–18) show an unmatched spin splitting (large Rashba parameter  $\alpha$ ), which is caused by an additional in-plane gradient of the potential;<sup>19</sup> the  $sp_z$  surface states in these alloys show the conventional topology of the Rashba model as well but with minor deviations (e.g., a nonzero but small  $P_z$  due to the in-plane gradient).

From the experimental and theoretical findings available so far one is lead to conclude that the spin topology imposed by the Rashba model shows up in a large number of systems, if not in all systems. In this paper, we show by first-principles calculations and two-photon photoemission (2PPE) experiments for the surface alloy Bi/Cu(111) that this topology cannot be taken for granted. Instead of the conven-

tional topology with oppositely rotating spins [Fig. 1(a)], we find momentum distributions with identical spin-rotation directions [Fig. 1(b)]. The origin of this effect is explained by the hybridization of surface states with different orbital character mediated by the spin-orbit interaction.

Our findings differ qualitatively from those in conventional Rashba systems. The momentum distribution of the latter comprises spin topologies with identical rotation direction as well but these are restricted to the low-density regime<sup>6</sup> (or region I in Ref. 20), i.e., to energies between  $\epsilon_0$  and the band extrema. This regime extents over 0.015 eV for the  $sp_z$  surface states in Bi/Cu(111).<sup>21</sup> But we find such topology in a 0.7 eV wide window in the high-density regime of the  $p_x p_y$  surface states. Note that the present findings are similar to those for topological metals and insulators.<sup>22,23</sup>

Previous studies of the Rashba effect at metal surfaces focused on occupied surface states since these can be accessed by angle-resolved photoelectron spectroscopy (ARPES).<sup>24</sup> These states are mainly of  $sp_z$  orbital character and thus agree with those of a 2DEG [see Ref. 10 for Au(111)]. As a consequence, their spin topology is consistent with that of the Rashba model [Fig. 1(a)].

In the Bi/Ag(111) and Pb/Ag(111) surface alloys, the adatoms induce also  $sp_z$  states but with larger splitting [as compared to Au(111)] and negative dispersion (effective mass  $m^* < 0$ ).<sup>16</sup> Further, there are indications for another mainly

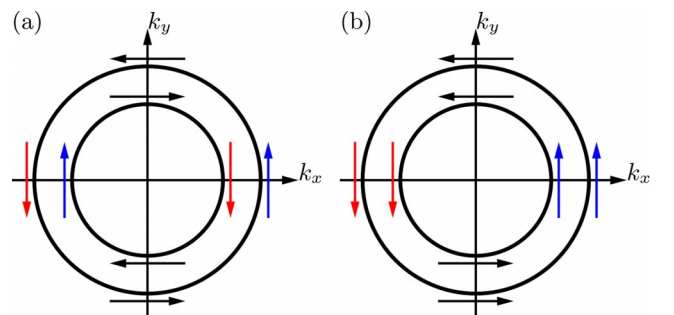


FIG. 1. (Color online) Spin topologies in a spin-orbit split 2DEG (schematic): (a) Conventional Rashba-type and (b) unconventional spin topology in the momentum distribution. The spin polarization of the “inner” and the “outer” state is represented by arrows.

unoccupied set of bands. Since these bands cross at energies  $\epsilon_0$  above the Fermi energy  $E_F$ , their splitting  $\Delta k$  could only be extrapolated from their occupied “tails.” First-principles calculations show that these states are of  $p_x p_y$  orbital character (i.e., oriented within the surface plane). Their occupied tails display the same spin topology as the  $sp_z$  states [Fig. 1(a)].

In the present work we focus on Bi/Cu(111) which shows a  $\sqrt{3} \times \sqrt{3}$ -R30° surface geometry,<sup>25</sup> such as Bi/Ag(111) and Pb/Ag(111). Consequently, the surface electronic structure of Bi/Cu(111) consists also of two sets of Rashba-split surface states, namely, the  $sp_z$  and the  $p_x p_y$  branch. As found by ARPES and scanning tunneling microscopy experiments,<sup>21,26</sup> the partially occupied  $sp_z$  branch extends to about  $E_F + 0.23$  eV and shows a Rashba splitting of  $\Delta k \approx 0.035$  Bohr<sup>-1</sup>.

## II. EXPERIMENTAL FINDINGS

In contrast to ARPES which maps the *occupied* states, we can additionally access the *unoccupied* states by angle-dependent 2PPE. Experimental details are as described in Ref. 27. The single-photon energy used in the 2PPE measurements was 3.1 eV, using off-normal-incident  $p$ -polarized light. Bi was deposited by thermal evaporation on the Cu(111) substrate kept at 500 K. The formation of the  $\sqrt{3} \times \sqrt{3}$ -R30° structure was checked by low-energy electron diffraction.

Angle-dependent 2PPE spectra were measured by rotating the sample around the axis perpendicular to the optical plane. The sample was oriented so that  $k_{\parallel}$  was measured in the plane containing the  $[111]$  and  $[1\bar{1}2]$  directions. The resulting experimental 2PPE intensity map is shown in Fig. 2. After the deposition of Bi, a reduction in the work function from about 4.9 eV for clean Cu(111) to below 4.4 eV is observed, as judged from the low-energy cutoff of the 2PPE spectrum at  $k_{\parallel}=0$  in Fig. 2. This makes possible the observation of additional unoccupied intermediate states in the energy region below 1.8 eV which cannot be excited above the work function on clean Cu(111) using 3.1 eV photons.

In the lower half of Fig. 2, at about 4.5 eV final-state energy, a pair of split bands is clearly visible. These bands belong to unoccupied states located one photon energy (3.1 eV) below the final-state energy; as will become clear from the comparison with theory, these bands originate from the  $p_x p_y$  surface states. They cross at  $\bar{\Gamma}$  at about  $E_F + (1.38 \pm 0.05)$  eV, and their maxima are shifted symmetrically from  $\bar{\Gamma}$  by about  $(0.06 \pm 0.01)$  Bohr<sup>-1</sup> [ $\Delta k \approx (0.12 \pm 0.02)$  Bohr<sup>-1</sup>] (Fig. 3).

In addition to the unoccupied states, the 2PPE experiment measures also the occupied states of  $sp_z$  character (see Fig. 4), which are excited by two photons to final-state energies near 6.2 eV in the upper half of Fig. 2. We note that a slightly increased intensity is also observed in the region extending to about 0.5 eV above the crossing point of the unoccupied split bands in Fig. 2. While no clearly dispersing bands can be observed experimentally, this intensity is consistent with the theoretical bands in Fig. 4 above 1.5 eV; their weak ex-

perimental intensity correlates with a comparably small theoretical spectral density.

The 2PPE intensity depends strongly on the emission angle, as can be seen by the pronounced intensity maximum at about 4.5 eV final-state energy and +5° emission angle (red spot in Fig. 2; note the comparably small intensity at -5°). Such features also appear also in the conventional (one-photon) photoemission from these surface alloys and can be explained by the transition matrix elements.

## III. THEORETICAL FINDINGS

To elucidate the dispersion and especially the spin topology of the unoccupied bands we performed first-principles electronic-structure calculations, in close analogy to our previous investigations on surface alloys (e.g., Ref. 16). The interatomic distances at the surface are obtained from total-energy minimization using the Vienna *Ab initio* Simulation Package.<sup>28</sup> Due to the much smaller lattice constant of Cu as compared to Ag ( $d_{\text{Cu-Cu}}=4.83$  Bohr and  $d_{\text{Ag-Ag}}=5.40$  Bohr), the Bi atoms are more relaxed outward (by 38% of the bulk interlayer distance of Cu,  $d_{\perp}=3.94$  Bohr) than in Bi/Ag(111). The optimum surface geometry serves as input for Korringa-Kohn-Rostoker (KKR) calculations. The electronic structure is analyzed in detail by means of the spectral density  $n(E, \mathbf{k})$ , which is computed from the Green's function in the relativistic layer-KKR method.  $n(E, \mathbf{k})$  is resolved with respect to site, spin, and angular momentum.

The spin-averaged spectral density of a Bi site shows the split  $sp_z$  and  $p_x p_y$  surface states (Fig. 4). Each branch comprises an “inner” band (with smaller  $|\mathbf{k}|$ ) and an “outer” band (with larger  $|\mathbf{k}|$ ). The  $sp_z$  bands cross at  $E_F + 0.1$  eV; their Rashba splitting is  $\Delta k = 0.10$  Bohr<sup>-1</sup> (Bi/Ag(111):  $\Delta k = 0.14$  Bohr<sup>-1</sup>). The  $p_x p_y$  bands cross at  $E_F + 1.4$  eV [experiment:  $E_F + (1.38 \pm 0.05)$  eV], with  $\Delta k = 0.08$  Bohr<sup>-1</sup> [experiment:  $\Delta k = (0.12 \pm 0.02)$  Bohr<sup>-1</sup>]. The theoretical results are thus consistent with the experimental findings and identify the split bands in experiment (Fig. 3) with the  $p_x p_y$  surface states. The spectral density becomes blurred in regions in which the surface states hybridize with Cu-bulk states. The dispersion of the two branches follows closely that imposed by the Rashba model [Eq. (1) with negative effective mass  $m^*$ ]. An exception, however, might be a “kink” in the inner  $p_x p_y$  band at  $(E, k) \approx (E_F + 0.6 \text{ eV}, \pm 0.12 \text{ Bohr}^{-1})$  (marked in Fig. 4).

The spin topology of the surface states is visualized by the difference  $n(E, \mathbf{k})|_{\uparrow} - n(E, \mathbf{k})|_{\downarrow}$  of the spectral densities, where  $\uparrow$  and  $\downarrow$  indicate the projection of the in-plane spin-polarization component normal to  $\mathbf{k}$  (Fig. 5; this  $\mathbf{P}$  component is prescribed by the Rashba model and is by far dominating). For the  $sp_z$  branch we find the expected conventional spin topology which is imposed by the Rashba model; the opposite spin-rotation direction of the two bands shows up at energies below the crossing at  $\bar{\Gamma}$  as a red-blue-red-blue color coding with increasing wave number [line a in Fig. 5; cf. Fig. 1(a)]. In contrast, the  $p_x p_y$  branch shows a red-red-blue-blue coding at, say,  $E_F + 1.0$  eV (line b in Fig. 5); thus these surface states have identical rotation direction [cf. Fig. 1(b)]. This finding is not consistent with the Rashba model: It

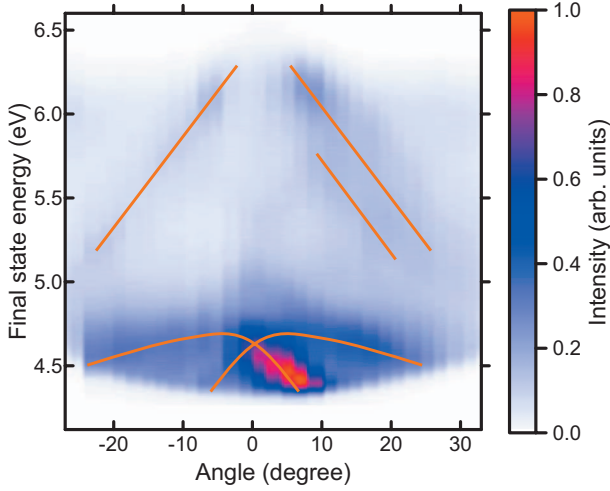


FIG. 2. (Color) Two-photon photoemission from Bi/Cu(111). The intensity for given final-state energy and emission angle is shown as color scale. The unoccupied  $p_x p_y$  surface states appear at about 4.5 eV. To guide the eye, orange lines highlight the dispersion of the electronic states.

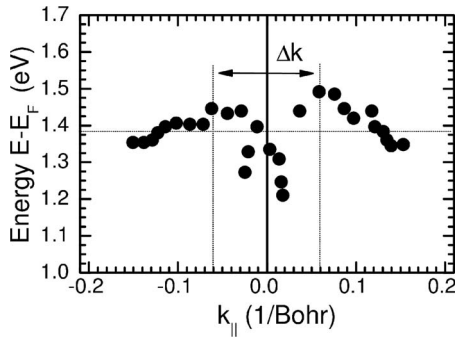


FIG. 3. Rashba splitting  $\Delta k$  in the unoccupied  $p_x p_y$  surface states of Bi/Cu(111), as obtained from two-photon photoemission experiments (Fig. 2).

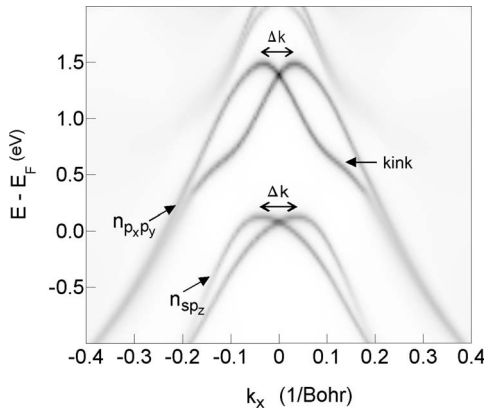


FIG. 4. Surface electronic structure of Bi/Cu(111) as obtained from first-principles calculations. The spectral density  $n(E, \mathbf{k})$  for a Bi site is depicted as gray scale (white=zero). The  $sp_z$  and the  $p_x p_y$  surface-state branches are indicated.

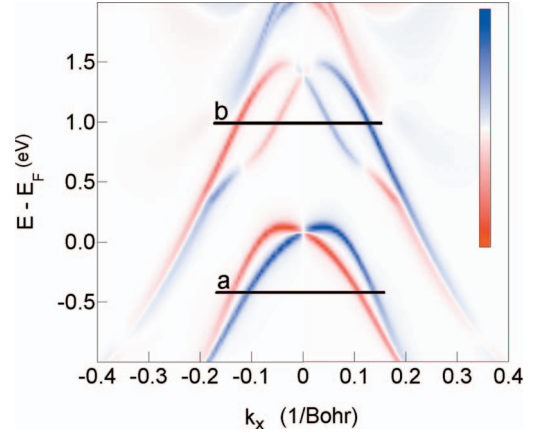


FIG. 5. (Color) Spin-resolved electronic structure of Bi/Cu(111) as obtained by first-principles calculations. The difference  $n(E, \mathbf{k})|_{\uparrow} - n(E, \mathbf{k})|_{\downarrow}$  of the spin-projected spectral densities for a Bi site is depicted as color scale (red=negative, white=zero, and blue=positive). The spin projection is in-plane and perpendicular to the wave vector. Horizontal lines are guides to the conventional (line a) and unconventional (line b) spin topology of the  $sp_z$  and the  $p_x p_y$  states, respectively.

appears that the spin polarization of the inner  $p_x p_y$  state is reversed in comparison to that of the inner  $sp_z$  state. It is important to note that at energies below the kink the spin polarization of this band has changed sign, e.g., at  $E_F + 0.2$  eV, and the conventional spin topology is restored; in other  $(E, \mathbf{k})$  regions its absolute value is as large as 90%.

Deviations from a smooth dispersion, as seen at the kink (Fig. 4), indicate hybridization of electronic states. A group-theoretical analysis shows that wave functions can be represented either as<sup>29,30</sup>

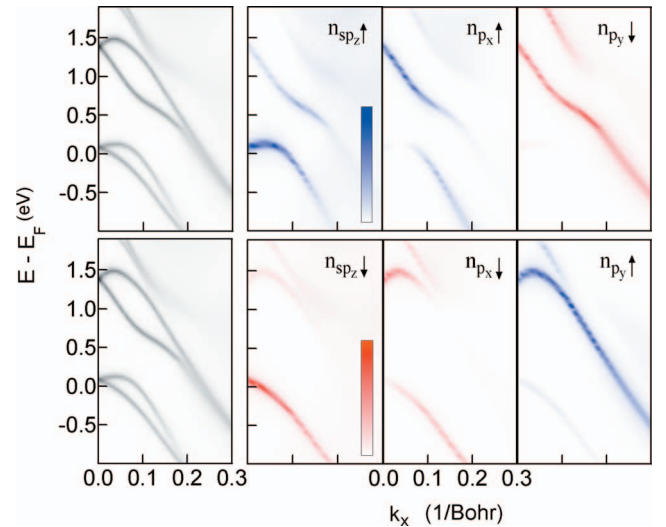


FIG. 6. (Color) Hybridization of surface states in Bi/Cu(111). The orbital- and spin-resolved spectral densities at a Bi site are depicted as color scales. The top [bottom] panels comprise contributions according to Eq. (2) [Eq. (3)]. All data share the same color scale, with white=zero and dark red (dark blue)=maximum spectral density (70 states/Hartree). The left panels display the total spectral density for comparison (in gray scale; cf. Fig. 4).



$$|\psi\rangle = |sp_z\uparrow\rangle + |p_x\uparrow\rangle + |p_y\downarrow\rangle \quad (2)$$

or as

$$|\psi\rangle = |sp_z\downarrow\rangle + |p_x\downarrow\rangle + |p_y\uparrow\rangle. \quad (3)$$

The spinors  $|\uparrow\rangle$  and  $|\downarrow\rangle$  are quantized with respect to the  $y$  axis. Both the outer  $sp_z$  band and the inner  $p_xp_y$  state belong to the representation of Eq. (2) and hence are allowed to hybridize. Thus, if the usually dominating  $|p_y\downarrow\rangle$  component of the inner  $p_xp_y$  state is surpassed by the  $|p_x\uparrow\rangle$  component, the spin polarization of this state changes sign. That this is indeed the case is seen by the  $|p_x\uparrow\rangle$  contribution to  $n(E, \mathbf{k})$ , which increases with energy (top row in Fig. 6). At the kink, where the inner  $p_xp_y$  band and outer  $sp_z$  band approach, both the  $|sp_z\uparrow\rangle$  and the  $|p_y\downarrow\rangle$  orbitals show a significant spectral density; the kink shape is thus attributed to the hybridization of these two bands. The inner  $sp_z$  and the outer  $p_xp_y$  states belong to the representation of Eq. (3) and hybridize as well but less due to their larger  $(E, \mathbf{k})$  “distance” (bottom row in Fig. 6).

Note that hybridization of orbitals with opposite spin is brought about only by SO coupling.<sup>31</sup> Further, the effect is not described by first-order perturbation theory in the SO interaction because this order would produce the spin splitting but not the hybridization.

The Dresselhaus effect could in principle produce a deviation from the Rashba-type spin topology.<sup>32</sup> A closer analysis, however, shows that it vanishes in the present case. Therefore, hybridization as a result of the spin-orbit interaction remains as the sole reason for the unconventional spin topology in Bi/Cu(111).

An important ingredient for the unmatched splitting found in these surface alloys is the in-plane gradient of the potential.<sup>15,19</sup> As the gradient perpendicular to the surface (along  $z$ ) produces the in-plane spin polarization ( $P_x$  and  $P_y$ ),

the in-plane gradient gives rise to a nonzero  $P_z$ . A  $p_xp_y$  surface state is expectedly more susceptible to the in-plane gradient than a  $sp_z$  surface state. Consequently, its  $P_z$  should be larger. Indeed,  $P_z$  of the  $p_xp_y$  states is negligibly for small  $|\mathbf{k}|$  but reaches 20% in absolute value for larger wave vectors ( $|\mathbf{k}| > 0.15 \text{ Bohr}^{-1}$ ). In contrast, the  $sp_z$  states have no significant  $P_z$ .

The demonstrated mechanism for changing the spin topology of the surface states in surface alloys is also present in Bi/Ag(111), as we have investigated theoretically as well (results not shown here). In comparison with Bi/Cu(111), the effect is less pronounced because hybridization of the  $sp_z$  and  $p_xp_y$  branches is decreased by the smaller outward relaxation of Bi.<sup>18</sup> Another aspect is that the surface states hybridize with Ag bulk states in a large  $(E, \mathbf{k})$  region due to projected bulk-band structure of Ag. As a consequence, they show no clear kink.

#### IV. CONCLUDING REMARKS

In summary, there is more to the spin-resolved electronic structure of surface states in surface alloys than first imagined. Although the basic properties are described by the standard Rashba model, additional effects (e.g., hybridization and the in-plane potential gradient) can change important features of the electronic states and their spin topology. In turn, there is the possibility to exploit these mechanisms in new spintronics devices and in new effects (e.g., Refs. 6 and 23).

Since hybridization is a general mechanism, the present effect can be important also in other systems, possibly at other high-symmetry points in the two-dimensional Brillouin zone or at other energies. It is therefore desirable to carry out spin-resolving experiments on the spin-orbit splitting of surface states.

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